Gotoh Laboratory (Special Issue on the Commemoration of the Fortieth Anniversary)

GOTOH LABORATORY (July 1947~)

Head: Dr. Rempei Gotoh

Prof. Rempei Gotoh succeeded Prof. Shinkichi Horiba in 1947. Sientific works carried out in this laboratory before 1951 from that time were reviewed in the Commemoration Volume for the Silber Juberee of the Institute for Chemical Research. Main subjects of the research since 1951 are as follows:

1. Dielectric properties of pure and disperse systems.
2. Infrared spectrosocpy of polar oragnic substances.
3. Surface and colloid chemistry.
4. Rheology.

Papers published during these fifteen years are reviewed briefly in the following.

I. Dielectric Properties of Pure and Disperse Systems

1. Spherical disperse system-emulsions: Dielectric properties of emulsions have been extensively studied. In oil-in-water-emulsions no dielectric dispersion was found and Bruggeman's equation hodls for both the dielectric constant and the conductivity of the system. With water-in-oil emulsions, however, a remarkable dielectric dispersion occurred and the limiting dielectric constant at high frequency was fitted by Bruggeman's equation. Bruggeman's equation was extended to a general spherical disperse system in which the disperse phase and medium have different dielectric constants and conductivities. The new equation derived from the theory of interfacial polarization in spherical disperse system holds for the dielectric relaxation as well as the static dielectric properties of a variety of emulsion over the whole concentration range of disperse phase.

2. Suspensions: Dielectric properties of solid powders dispersed in liquid paraffin were studied. Unlike the results on emulsions, the dielectric dispersion due to the interfacial polarization was not found, but moisture adsorbed on solid powder particles contributed to a relaxation of the wedge type.

3. Binary mixtures: In hexane-nitrobenzen mixture either an emulsion or a molecular solution was realized under the condition of composition of a mixture and temperature. The dielectric constants of this particular system were discussed, based on dielectric theories of a molecular solutions and a disperse system.

4. Polar Liquids: Dielectric porperties of pure low-molecular weight polyethylene glycols were investigated over a wide range of frequency. The static dielectric constants of the glycols showed typical dielectric behavior of hydrogen-bonded liquids. The dielectric relaxation in the glycols was observed at microwave frequencies. A striking feature in the relation between relaxation time and the chain length was discussed in terms of flexibility of the molecular chain.

II. Infrared Spectroscopy of Polar Organic Substances

(1) Surface activities and molecular Structures

(A) Oxydation of liquid paraffin: Infrared absorption of liquid paraffin heated in the atomosphere of oxygen and nitrogen were measured at various temperatures. While vinyl compounds were decteted in nitrogen at above 300°C, formation of OH and CO radicals appeared in oxygen at above 150°C. Surface activities were observed only for the specimens heated in oxygen atomsphere.

(B) Inductive effect of polar substituents on CH stretching vibration: Infrared absorption studies were carried out of the CH stretching frequencies for homologous series of aliphatic alcohols, fatty acids, alkyl bromides as well as n-hydrocarbons. It was pointed out that the methyl stretching frequencies ν decrease with the carbon chain length, n, following the relation;

$$\nu - \nu_0 = Ae^{-Bn},$$

where ν_0 is the methyl frequency of saturated hydrocarbon and both A and B are experimental constants. Above relation was derived theoretically and interpreted in terms of inductive effect of electronegativities of ploar substituents.

(2) Application of polarized infrared spectroscopy: Molecular structure and orientation of organic substances were investigated by means of polarized infrared spectroscopy. A new method was proposed for the determination of the direction of the transition moments with a given molecular vibration, and applied to molecular crystals with C_s, S_{2h} or C_2 symmetry. A differential method of polarized infrared spectroscopy was devised and applied to the study of orientation of polymer molecules such as vulcanized natural rubber, polyethyleneand polyvinyl chloride during elongation as well as stress relaxation.

III. Surface and Colloid Chemistry

1 Interaction between dyestuffs and surfactants: Chromatography and capillary analysis were applied to the study of the interaction between dyestuffs and surfactants, especcially non-ionic surfactants. A theory of capillary analysis was proposed and formation of complexes of dyes and surfactant as well as association of dyes and surfactants were discussed. Interaction between dyes and DNA (deoxyribonucleic acid) were also discussed.

2 Electrocapillary phenomena:

(1) Theory of coagulation of colloids and coalescence of mercury droplets: The potential ranges of polarization of a pair of mercury droplets, over which the two droplets coalesced, were measured as functions of ionic concentrations for various electrolytes. The condition of coalescence was proved to be in quantitative agreement with the Verwey-Overbeek theory of coagulation of hydrophobic colloids.

(2) Electrocapillary curves of oil-water interfaces: Electrocapillary curves were obtained for the systems of organic solvents in contact with aqueous solutions.

The electrocapillary curve depended upon the ionic type of the surface active agents in the oil phase. The experimental results were discussed with respect to the ionic structure of the electric double layer at the oil-water interface.

IV. Rheology

1 Viscoelastic behaviors of colloidal materials:

Viscoelasticities of asphalts and bentonite gels were measured by means of a cone and plate type viscometer. Viscosity coefficients, delayed elastic compliance and the retardation spectra of asphalts were obtained from the strain-time and recovery curves at various temperatures. Bentonite gels showed viscoelastic behavior between two limits of shearing stress. Characteristic slip fracture were observed above critical shearing stress, which depended upon the concentration of bentonite.

2 Mechanical fracture of colloidal materials:

(1) Brittle velosity: Type of mechanical fracture or breakdown of viscous materials such as rosin, asphalts and plastisized polymers were examined at various rate of extension and temperatures. It was found that the critical velosity for brittle fracture and for dropping break-down increased exponentially with increasing temperature. Creeping or spinnable extension was observed between those two limiting conditions.

(2) Slip fracture and shear strength of bentonite gels: Shear modulus and shear strength for slip fracture were measured by various methods over the wide range of concentration of bentonite. Shear modulus, G, showed characterestic dependency on the concentration similar to those of gel elasticity of high polymers. It was found that the shear strength F_0 was related to the shear strength as follows:

$$F_0 = \nu_0 G,$$

where ν_0 is the critical strain and took almost theoretical values ranging 1/10—1/30.

Publications

(* indicates an article published in Japanese.)

I. Dielecric Properties of Pure and Disperse Systems

1. N. Koizumi; Complex Dielectric Constants of Some Aliphatic Alcohols at 9733 mc/sec. *J. Chem. Physics,* **21,** 1898 (1953).
2. N. Koizumi and T. Hanai; Dielectric Constants of Some Alcohols at Low Frequencies. *Bull. Inst. Chem. Res., Kyoto Univ.,* **33,** 14 (1955).
3. N. Koizumi and T. Hanai; Dielectric Properties of Lower-Membered Polyethylene Glycols at Low Frequencies. *J. Phys. Chem.,* **60,** 1496 (1956).
4. T. Uchida, Y. Kurita, N. Koizumi and M. Kubo; Dipole Moments and the Structures of Polyethylene Glycols. *J. Polymer Sci.,* **21,** 313 (1956).
5. N. Kiozumi; Dielectric Properties of Polyethylene Glycosl at Microwave Frequencies. *J. Chem. Physics,* **27,** 625 (1957).
6. R. Gotoh, T. Hanai and N. Koizumi; Influence of Moisture upon the Dielectric Properties of Solid Powders Disperesed in Liquid Paraffin. *Nature,* **181,** 406 (1958).

7. T. Hanai, N. Koizumi and R. Gotoh; State of Dispersion and Dielectric Constant of Nitrobenzene-Hexane mixture. *Nippon Kagaku Zasshi,* **80,** 17 (1959).*
8. T. Hanai, N. Koizumi and R. Gotoh; Dielectric Properties of Emulsions. I Dielectric Constants of O/W Emulsion. *Kolloid-Z.* **167,** 41 (1959).
9. T. Hanai, N. Koizumi, T. Sugano and R. Gotoh; Dielectric Properties of Emulsions. II Electrical Conductivities of O/W Emulsions. *Kolloid-Z.* **171,** 20 (1960).
10. T. Hanai; Theory of the Dielectic Dispersion due to the Interfacial Polarization and its Application to Emulsions. *Kolloid-Z.* **171,** 23 (1960).
11. T. Hanai; Dielectric Properties of Emulsions. III Dielectric Behabior of W/O Emulsions *Kolloid-Z.* **177,** 57 (1960).
12. T. Hanai, N. Koizumi and R. Gotoh; Temperature Dependence of Dielectric Constants and Dipole Moments in Polar Liquids. *Bull. Inst. Chem. Res., Kyoto Univ.,* **39,** 195 (1961).
13. T. Hanai; Dielectric Theory on the Interfacial Polarization for Two-Phase Mixtures. *Bull. Inst. Chem. Res., Kyoto Univ.,* **39,** 341 (1961).
14. T. Hanai; A Remark on the "Theory of the Dielectric Dispersion due to the Interfacial Polarization". *Kolloid-Z.,* **175,** 61 (1961).
15. T. Hanai, N. Koizumi and R. Gotoh; Dielectric Properties of Emulsions IV Dielectric Behavior of Nitrobenzene-Water Emulsions. *Kolloid-Z.,* **184,** 143 (1962).
16. N. Koizumi and T. Hanai; A Low Frequency Selective Amplifier. *Bull. Inst. Chem. Res., Kyoto Univ.,* **40,** 188 (1962).
17. T. Hanai, N. Koizumi and R. Gotoh; Dielectric Constants of Emulsions. *Bull. Inst. Chem. Res., Kyoto Univ.,* **49,** 240 (1962).

Reviews

1. N. Koizumi; Applications of Microwave. *High Polymers, Japan,* **4,** 6No. 37 158 (1955).*
2. R. Gotoh, N. Koizumi and T. Hanai; Dielectric Constants of Colloidal Dispersions. *Kagaku (Kyoto)* **13,** 710 (1958).*
3. N. Koizumi; MKS Unit Systems. *Chemistry and Industry (C.S.J.)* **12** No. 9 40 (1959).*

Book

1. T. Hanai, N. Koizumi and R. Gotoh; The Dielectric Behavior of Emulsions "Emulsion Rheology" p. 91–113 (1963), Pergamon Press, Oxford.

II. Infrared Spectroscopy of Polar Organic Substances

1. R. Gotoh, T. Takenaka and S. Hayashi; Infrared-spectroscopic Studies on Oxydation of Liquid Hydrocarbons. *Kogyo Kagaku Zasshi,* **63,** 729 (1960).*
2. R. Gotoh and T. Takenaka; Inductive Effect of Polar Substituents on Carbon-Hydrogen Stretching Vibration of Aliphatic Hydrocarbons. *Nippon Kagaku Zasshi,* **81,** 1504 (1960)*; *Bull. Inst. Chem. Res., Kyoto Univ.,* **39,** 202 (1961).
3. T. Takenaka; Inductive Effect of Polar Substituents on CH Symmetric Deformation Frequencies of Aliphatic Hydrocarbons. *Nippon Kagaku Zasshi,* **82,** 1309)(1961).*
4. T. Takenaka; Inductive Effect of Adjacent Groups on the Symmetrical CD Deformation Frequencies. *Nippon Kagaku Zasshi,* **83,** 267 (1962).*
5. T. Takenaka; Inductive Effect of Adjacent Groups on Rocking Frequencies of Methyl Groups. *Nippon Kagaku Zasshi,* **83,** 997 (1962).*
6. M. Tamura, H. Haneda, J. Noguchi and S. Hayashi; Infrared Spectra of Some Photographic Stabilizers adsorbed on Silber Bromide. *J. Phys. Chem.,* **66,** 559 (1962).
7. T. Takenaka and R. Gotoh; Inductive Effect of Adjacent Groups on the Symmetrical Deformation and the Rocking Frequencies of Methyl Groups. *Bull. Inst. Chem. Res., Kyoto Univ.,* **40,** 272 (1962).
8. R. Gotoh and T. Takenaka; Infrared Absorption Spectra of Some Monovalent Metal Salts of Fatty Acids. *Nippon Kagaku Zasshi,* **84,** 392 (1963).*
9. T. Takenaka and S. Hayashi; Vibrational Spectra of Tetracyanoethylene. *Bull. Chem. Soc., Japan,* **37,** 1216 (1964).

10. S. Hayashi; Polarized Infrared Spectra of Benzene Derivatives. *Nippon Kagaku Zasshi,* **85,** 186 (1964).*
11. S. Hayashi; Polarized Infrared Spectra of Succinimde. *Nippon Kagaku Zasshi,* **86,** 27 (1965).*
12. S. Hayashi; Polarized Infrared Spectra of Acetanilide. *Nippon Kagaku Zasshi,* **86,** 790 (1965).*
13. S. Hayashi; Polarized Infrared Spectra of Planar Molecules. *Bull. Inst. Chem. Res., Kyoto Univl.,* **43,** 355 (1965).
14. R. Gotoh, T. Takenaka and N. Hayama; Simultaneous Measurements of Stress and Infrared Dichroism on Polymers: Stress Relaxation of Vulcanized Natural Rubber. *Kolloid-Z. Z.f. Polymere,* **205,** 18 (1965); *Nippon Kagaku Zasshi,* **86,** 1137 (1965);* *Bull. Inst. Chem. Res., Kyoto Univ.,* **43,** 369 (1965).
15. R. Gotoh, T. Takenaka, J. Umemura and S. Hayashi; Simultaneous Mearsurements of Stress and Infrared Dichroism of Inflated Polyethylene Films. *Bull. Inst. Chem. Res., Kyoto Univ.,* **44,** 286 (1966).
16. S. Hayashi and N. Kimura; Infrared Spectra and Molecular Configuration of Benzoic Acid. *Bull. Inst. Chem. Res., Kyoto Univ.,* **44,** 235 (1966).

Review

T. Takenaka: "Strudies on the State of Adsorption by Infrared Spectroscopy". *Surface (Hyouen)* **4,** No. 5, 301, No. 6, 373 (1966).*

Book

T. Takenaka: "Instrumental Analysis"-Chapter 10. Chemical Infrared Spectroscopy. Ed. by Japan Society of Chemical Analysis. (1960).*

III. Surface and Colloid Chemistry

1. R. Gotoh, N. Koizumi, N. Hayama and T. Sugano; Molecular Weight of Polyoxyethylene Glycols and their Derivatives. Cryorcopic Measurements and Solvent Effcets. *Nippon Kagaku Zasshi,* **74,** No. 12, 994 (1953)*; *Bull. Inst. Chem. Res., Kyoto Univ.,* **31,** 285 (1953).
2. R. Gotoh, T. Sugano and N. Koizumi; Micelle Formation of Non-ionic Surfactants Properties of Aqueous Solution of Polyoxyethylene monoalkyl Ether. *Nippon Kagaku Zasshi,* **75,** 73 (1954)*; *Bull. Inst. Chem. Res., Kyoto Univ.,* **31,** 305 (1953).
3. R. Gotoh and N. Hayama; Chromatographic Investigation of the Interaction between Dyestuffs and Surfactants. *Nippon Kagaku Zasshi,* **84,** 104 (1963).*
4. T. Sugano; Influences of Additives on the Cloud Point of Nonionic Surface Active Agents. *Nippon Kagaku Zasshi,* **84,** 520 (1963).*
5. N. Hayama; Theory of Capillary Analysis. *ibid.,* **84,** 943 (1963).*
6. N. Hayama; Interaction between Dyes and Non-ionic Surfactants. *ibid.,* **84,** 948 (1963).*
7. N. Hayama; Interaction between Dyes and Deoxyribonucleic Acid. *ibid.* **84,** 953 (1963).*
8. N. Hayama; Theory of Capillary Analysis and its Application to Dyeing Chemistry. *Bull. Inst. Chem. Res., Kyoto Univ.,* **42,** 401 (1964).
9. A. Watanabe and R. Gotoh; On the Theory of Coagulation and the Coalescence of Mercury Droplets in Aqueous Solutions. *Kolloid Z. Z.f. Polymere,* **191,** 36 (1963).
10. R. Gotoh and A. Watanabe; On the Coagulation Thoery of Colloids and Coalescence of Mercury Droplets in Aqueous Solutions. *Nippon Kagaku Zasshi,* **84,** 480 (1963).*
11. A. Watanabe, M. Matsumoto and R. Gotoh; Influence of Surface Active Materials on the Coalescence of Mercury Droplets in Aqueous Solutions. *ibid.* **85,** 730 (1964.)*
12. A. Watanabe, M. Matsumoto and R. Gotoh; On the Coalescence of Mercury Droplets in Aqueous Solutions. *Bull. Inst. Chem. Res., Kyoto Univ.,* **42,** 389 (1964).
13. A. Watanabe, M. Matsumoto and R. Gotoh; The Coalescence of Mercury Droplets in Aqueous Solution in the Presence of Surface Active Materials. *Kolloid Z., Z.f. Polymere,* **201,** 147 (1965).
14. A. Watanabe, M. Matsumoto and R. Gotoh; Electro-capillary Curves of Oil-Water Systems

containing Surface Active Agents. *Nippon Kagaku Zasshi,* **87,** 941 (1966).*

15. A. Watanabe, M. Matsumoto and R. Gotoh; The Electrocapillarity of Oil-Water Interfaces. *Bull. Inst. Chem. Res., Kyoto Univ.,* **44,** 273 (1966).

Reviews

1. R. Gotoh: Surface Activity and Molecular Structures. (*Modern Chemistry and its Application*) No. 13, 72 (1961).*
2. R. Gotoh: Coagulation and Dispersion by Surfactants. *J. Japan Soc. Col. Mat.,* **35,** 444 (1962).*
3. R. Gotoh: Interaction between Surfactants and Dyes. *Oil* (*Yushi*)) **17,** No. 12 24 (1964.).*
4. A. Watanabe; On the Application of the Theory of the Electrical Double Layer in Colloidal Phenomena, *Rev. of Polarography* (*Japan*) **10,** 175 (1962).*
5. A. Watanabe; The Coagulation of Colloids and Related Phenomena, *Pigment* (*Ganryo*) **7,** 886, 915, 941 (1963).*
6. A. Watanabe; The Coagulation of Colloidal Powders, *J. Japan Soc. of Powder Metallurgy,** **11,** 73 (1964).*
7. A. Watanabe, Electrical Phenomena at Solid and Liquid Interfaces, *Colour Material* (*Shikizai Kyokai Shi*)* **38,** 529 (1965).*
8. A. Watanabe; Introduction to the Interfacial Electrical Phenomena, *Surface* (*Hyomen*) **3,** 416, 498, 564, 641, 712, 781 (1965).*
9. A. Watanabe; On the Coagulation of Powders, *Powder Engineering* (*Funtai Kogaku*) **3,** 29 (1966).*
10. A. Watanabe; The Phenomenology of Solid-liquid Interfaces, *Technical Chemical Engineering* (*Kagaku Kikai Gijutsu*) **18,** 1 (1966)*, Maruzen Book Co., Tokyo.

Books

1. R. Gotoh and T. Sugano: "Experimental Chemistry" Vol. 7. Chap. 4. Solution Properties of Surface Active Agent. Maruzen (1956).*
2. R. Gotoh: "Dyeing Process" Chap. 2. Physico-chemical Properties of Dye-Solutions. Kyoritsu Pub. Co. (1958).*
3. R. Gotoh and A. Watanabe (Translation): "Colloid Chemistry" by M.J. Vold and K.D. Vold; Kyoritsu Pub. Co. (1966).*

IV. Rheology

1. R. Gotoh, H. Aida, S. Hayashi and N. Hirai; Brittle Fracture and Spinnability of Viscous Materials. *Bull. Inst. Chem. Res., Kyoto Univ.,* **35,** (1957); *Rheologica Acta,* **1,** 213 (1958).
2. H. Aida; Brittle Fracture of Asphalts. *Nippon Kagaku Zasshi,* **82,** 1134 (1961).*
3. H. Aida; Heterogeneous Properties in the Fracture. *ibid.* **82,** 1139 (1961).*
4. H. Aida; Viscoelastic Properties of Asphalts. *J. Japan Petroleum Institute,* **4,** No. 11, 19 (1961).*
5. H. Aida, T. Hanai and R. Gotoh; Viscoelastic Properties of Bentonite Pastes. *Nippon Kagaku Zasshi,* **83,** 536 (1962).*
6. R. Gotoh and N. Hayama; Chemical Creep of Polyester Film. *Kogyo Kagaku Zasshi,* **68,** 998 (1965).*
7. R. Gotoh and K. Shimizu; Slip Fracture and Shear Strength of Bentonite Gels. *Bull. Inst. Chem. Res., Kyoto Univ.,* **43,** 380 (1965).

Reviews

1. R. Gotoh and H. Aida; Fracture and Strength of Polymer Materials. *Kogyo Kagaku Zasshi,* **59,** 768 (1956).*
2. R. Gotoh and M. Koyama (Translation): "Surface Scensitive Mechanical Properties" (Review), by A.R.C. Westwood; *Surface* (*Hyomen*) **4,** 691 (1966).*

Book

R. Gotoh, N. Hirai and T. Hanai: "Rheology and Its Applications" Kyoritsu Pub. Co. (1962).*